

CLAIMS

1. Process for the preparation of a haloalkyldialkylhalosilane of formula
 5 (I):



by hydrosilylation reaction of a reaction medium comprising:

- a silane of formula (II):

$$\text{Hal}-(\text{R}^2\text{R}^3)\text{Si}-\text{H}$$
- 10 ▪ and an alkenyl halide of formula (III):

$$\text{CH}=\text{CH}-(\text{CH}_2)_{s-2}\text{Hal}$$
- in the presence of a catalytically effective amount of a hydrosilylation catalyst based on iridium in the oxidation state I or III,

in which formulae (I), (II), (III):

- 15 - the symbol Hal represents a halogen atom chosen from the chlorine, bromine and iodine atoms,
- the symbols R^2 et R^3 , which are identical or different, each represent a monovalent hydrocarbon group chosen from a linear or branched alkyl radical having from 1 to 6 carbon atoms and a phenyl radical, and
- 20 - s represents an integer between 2 and 10 inclusive,

the said process being characterized in that at least one auxiliary in the free or supported state selected from the group of compounds consisting of:

- 25 > (i) ketones,
- > (ii) ethers,
- > (iii) quinones,
- > (iv) anhydrides,
- > (v) unsaturated hydrocarbon compounds (UHC) having an aromatic nature and/or comprising at least one C=C double bond and/or at least one C≡C triple bond, it being possible for these unsaturated bonds to be conjugated or nonconjugated, the said UHCs being linear or cyclic (mono- or polycyclic), having from 4 to 30 carbon atoms, having from 1 to 8 ethylenic and/or acetylenic unsaturations and optionally comprising one or more heteroatoms,
- 35 > (vi) and their mixtures,

is added to the reaction medium, with the condition according to which, when the auxiliary comprises one or more UHCs as defined above, then this (these) UHC(s) is (are) mixed with at least one other auxiliary other than a UHC.

5 2. Process according to Claim 1, characterized in that use is made of a catalyst based on iridium in the oxidation state I, in the structure of which each iridium atom corresponds to the complex form of the $\text{Ir}(\text{L})_3\text{X}$ type where the symbols **L** and **X** have the definitions given in the work "Chimie Organométallique" [Organometallic Chemistry] by Didier Astruc, published in 2000
10 by EDP Sciences (cf. in particular page 31 et seq.).

3. Process according to Claim 2, characterized in that the catalyst corresponds to the formula:



in which:

- the symbol R^4 represents either a monodentate ligand L, and in this case $x = 2$, or a bidentate ligand $(L)_2$, and in this case $x = 1$, and
- the symbol R^5 represents either Hal, which represents a halogen atom chosen from the chlorine, bromine and iodine atoms, and in this case $y = 2$, or a ligand of type LX, and in this case $y = 1$.

4. Process according to Claim 3, characterized in that, in the formula (IV):

- R⁴ is a ligand comprising at least one C=C double bond and/or at least one C≡C triple bond, it being possible for these unsaturated bonds to be conjugated or nonconjugated, the said ligand being linear or cyclic (mono- or polycyclic), having from 4 to 30 carbon atoms, having from 1 to 8 ethylenic and/or acetylenic unsaturations and optionally comprising one or more heteroatoms, and
- R⁵, in addition to Hal, can also represent a ligand LX, such as in particular a ligand derived from acetylacetone, from a β-ketoester, from a malonic ester or from an allyl compound.

5. Process according to Claim 1, characterized in that the auxiliary is
35 introduced into the reaction medium in the free state and according to a molar

ratio, with respect to the iridium metal, of at least 0.2, preferably of at least 1 and more preferably of at least 100.

6. Process according to Claim 1, characterized:

- 5 ➤ in that the auxiliary comprises at least one compound selected from the group of the UHCs (v), taken by themselves or as a mixture with one another,
- and in that the concentration of catalyst (preferably IV) is such that the iridium/silane of formula (II) molar ratio is less than or equal to 400×10^{-6} , preferably less than or equal to 200×10^{-6} and more preferably still less than or equal to
- 10 50×10^{-6} .

7. Process according to any one of Claims 1 to 6, characterized in that the auxiliary is selected from the group consisting of:

cyclohexanone, 2-cyclohexen-1-one, isophorone, 2-benzylidenecyclohexanone,

15 3-methylene-2-norbornanone, 4-hexen-3-one, 2-allylcyclohexanone, 2-oxo-1-cyclohexanepropionitrile, 2-(1-cyclohexenyl)cyclohexanone, monoglyme, ethylene glycol divinyl ether, ethyl ether, benzoquinone, phenylbenzoquinone, maleic anhydride, allyl succinic anhydride, 3-benzylidene-2,4-pentadione, phenothiazine, (methylvinyl)cyclotetrasiloxane (vinylated D4), 4-phenyl-3-butyne-2-one, 1,3-

20 butadiene, 1,5-hexadiene, 1,3-cyclohexadiene, 1,5-cyclooctadiene (COD), 1,5,9-cyclododecatriene, divinyltetramethylsiloxane (DVTMS), norbornadiene and their mixtures.

8. Process according to any one of Claims 1 to 7, characterized in that the

25 auxiliary is a mixture (vi) comprising at least one UHC (v), preferably COD, and at least one ketone (i), preferably cyclohexanone, and/or at least one ether (ii) and/or at least one quinone (iii).

9. Process according to Claim 8, characterized in that the concentration of

30 catalyst, preferably of formula (IV), is such that the iridium/silane of formula (II) molar ratio is less than or equal to 100×10^{-6} , preferably less than or equal to 60×10^{-6} , and more preferably still is between 40×10^{-6} and 1×10^{-6} .

10. Process according to Claim 8, characterized in that the components of the mixture (vi), UHC/(i) and/or (ii) and/or (iii), are present in the reaction medium when the reaction begins.

5 11. Process according to any one of Claims 1 to 10, characterized in that the product of formula (I) is 3-chloropropyldimethylchlorosilane, the product of formula (II) is dimethylhydrochlorosilane and the product of formula (III) is allyl chloride.

10 12. Catalytic system for the preparation of a haloalkyldialkylhalosilane of formula (I):



by hydrosilylation reaction of a reaction medium comprising:

- a silane of formula (II):



- and an alkenyl halide of formula (III):



in which formulae:

- the symbol Hal represents a halogen atom chosen from the chlorine, bromine and iodine atoms,
- the symbols R^2 et R^3 , which are identical or different, each represent a monovalent hydrocarbon group chosen from a linear or branched alkyl radical having from 1 to 6 carbon atoms and a phenyl radical, and
- s represents an integer between 2 and 10 inclusive,

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characterized in that it comprises:

- 1- a hydrosilylation catalyst based on iridium in the oxidation state I, in the structure of which each iridium atom corresponds to the complex form of the $\text{Ir}(\text{L})_3\text{X}$ type where the symbols L and X have the definitions given in the work "Chimie Organométallique" [Organometallic Chemistry] by Didier Astruc, published in 2000 by EDP Sciences (cf. in particular page 31 et seq.), this catalyst preferably corresponding to the formula:

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in which:

- the symbol R^4 represents either a monodentate ligand L, and in this case $x = 2$, or a bidentate ligand $(L)_2$, and in this case $x = 1$, and
- the symbol R^5 represents either Hal, Hal representing a halogen atom chosen from the chlorine, bromine and iodine atoms, and in this case $y = 2$, or a ligand of type LX, and in this case $y = 1$,

-2- and at least one auxiliary in the free or supported state selected from the group of compounds consisting of:

- (i) ketones,
- (ii) ethers,
- (iii) quinones,
- (iv) anhydrides,
- (v) unsaturated hydrocarbon compounds (UHC) having an aromatic nature and/or comprising at least one C=C double bond and/or at least one C≡C triple bond, it being possible for these unsaturated bonds to be conjugated or nonconjugated, the said UHCs being linear or cyclic (mono- or polycyclic), having from 4 to 30 carbon atoms, having from 1 to 8 ethylenic and/or acetylenic unsaturations and optionally comprising one or more heteroatoms,
- (vi) and their mixtures,

with the condition according to which, when the auxiliary comprises one or more UHCs as defined above, then this (these) UHC(s) is (are) mixed with at least one other auxiliary other than a UHC.